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CALCULATION OF THE EQUILIBRIUM STRUCTURES OF

SMALL METAL ATOM CLUSTERS Semiannual HC A03/mF A01

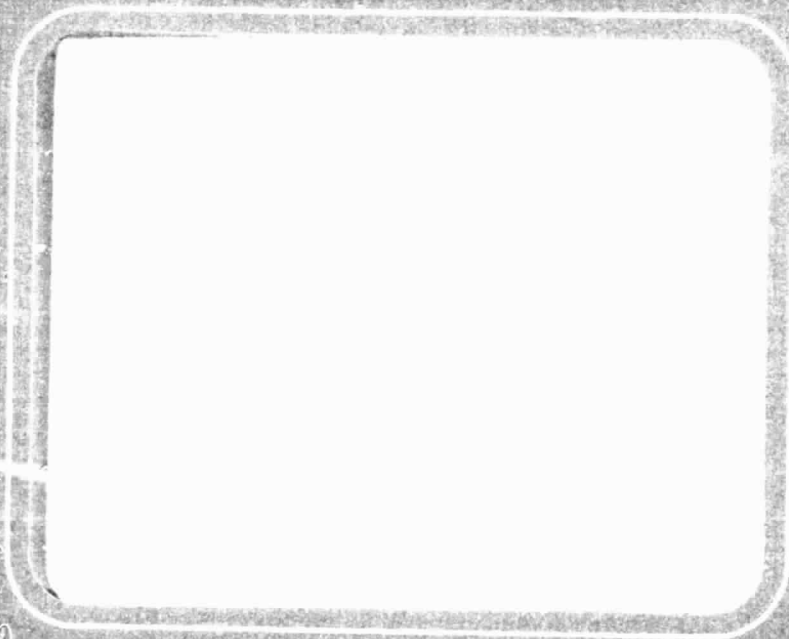
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Report



SEMI-ANNUAL PROGRESS REPORT

on

QUANTUM CHEMICAL CALCULATION OF THE EQUILIBRIUM
STRUCTURES OF SMALL METAL ATOM CLUSTERS

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER

October 23, 1981

by

Luis R. Kahn

Grant NSG-2027

This covers the period April 15, 1981 to October 30, 1981

BATTELLE
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October 23, 1981

Dr. David Cooper
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Dear Dave:

Enclosed are three (3) copies of the semi-annual progress report of work on "Quantum Chemical Calculation of the Equilibrium Structures of Small Metal Atom Clusters" under NASA Grant NSG-2027.

Best regards,

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EXECUTIVE SUMMARY

Clusters of metal atoms are of importance as models of substrates in studies of Chemisorption on metal surfaces and of catalysis of chemical reactions; they are also of increasing interest as novel molecular species in their own right that, surrounded by certain ligands, are possibly a whole new class of catalysts. Moreover, clusters of metal atoms are useful as a prototype atomic-level host systems for the development and testing of models of interatomic forces. These interatomic forces are a basic ingredient to the much more complex atomic modeling of the mechanical properties of metals that are used to address important materials problems such as the effect of hydrogen on crack propagation.

The approach we have taken to the study of metal atom clusters is based on the application of ab initio quantum mechanical approaches. This interim report discusses our current research effort in the application of these methods. Because these large "molecular" systems pose special practical computational problems in the application of the quantum mechanical methods, there is a special need to find simplifying techniques that do not compromise the reliability of the calculations. Our current research is therefore directed towards various aspects of the implementation of the Effective Core Potential (ECP) technique for the removal of the metal atom core electrons from the calculations. This interim report discusses our recent progress in this area.

During this reporting period we have developed a reformulation of the ECP molecular integral formulae to bring out the shell characteristics in the formulae. This is an important first step towards fulfilling the increasing need, especially for the metal atom clusters, to speed up the computation of the ECP integrals. Also during this reporting period, we have completed and published work on the relationships among the derivatives of the molecular integrals that extends some of the techniques pioneered by Komornicki for the calculation of the gradients of the electronic energy. Finally, during this reporting period, we have discovered a new formulation of the ECP approach that quite naturally unifies the various state-of-the-art "shape- and Hamiltonian-consistent" techniques.

QUANTUM CHEMICAL CALCULATION OF THE EQUILIBRIUM STRUCTURES OF SMALL METAL ATOM CLUSTERS

by

Luis R. Kahn

INTRODUCTION

The goal of this research is to gain quantitative fundamental understanding about the properties of clusters of metal atoms. The increasing interest in these novel "molecular" species stems from their use to model substrates in the study of chemisorption, and from the prospects that such studies will yield the long-sought understanding of the mechanisms of heterogeneous catalysis of chemical reactions. Moreover, these metal atom clusters surrounded by carbonyl groups, are indeed being thought of as new types of catalysts in their own right. In every case, however, there is still very little known yet about these interesting new molecular species. Since the atomic level properties of these clusters are not yet readily available from experiment, the most reliable approach to their determination lies in the development and application of predictive ab initio quantum mechanical approaches.

This interim report describes our current research effort designed to continue the development of a reliable, more accurate, and more efficient quantum mechanical method necessary for the calculation of the properties of clusters of metal atoms. The method deals with the important simplification in the quantum mechanical calculation of metal atom clusters of the removal of the metal atom core electrons from the calculations. The method being pursued is based on the Effective Core Potential (ECP) approach to simulate the effect of the core electrons on the valence electrons.⁽¹⁾ So far in this project we have concentrated on the computer programs that will allow us to carry out the quantum mechanical calculations, on possible simplifications in these calculations, on the reformulation of the ECP integral computation as efficiency is becoming of the essence for these metal atom cluster calculations, and, finally, on the continually expanding need to refine the ECP's themselves. In the following section we expand on the progress made during these last six months, while the Appendix contains a reprint of a publication derived from work on this NASA Grant.

SCIENTIFIC PROGRESS

Evaluation of Matrix Elements of the ECP

The interface of the program to evaluate the SPDF ECP molecular integrals with Komornicki's programs has proven to be straightforward. A comparison of the interface codes written independently by both S. Kato and ourselves shows essential agreement. The evaluation of the gradients of the ECP integrals, in turn, reduces to a matter of calling for special combinations of ECP integrals obtained from the programs thus far interfaced. Indeed, S. Kato has recently added this ECP capability to Komornicki's programs. One of the advantages of this implementation of the gradient of the ECP's over that of the comparable implementation of the SPD ECP's in the well-known GAUSSIAN 80 package of programs is that the calculation of the gradient is not restricted to those cases for which only s and p functions appear in the basis set. Plans have been made to use this SPDF ECP enhanced version of Komornicki's programs to investigate the structure of Cs atom clusters in collaboration with B. Laskowsky because it has become clear that there is a strong common interest in these problems.

As part of an effort to contribute to the gradient evaluation technology, a paper has been submitted and accepted for publication that discusses the relationships among derivatives of the molecular integrals arising from the transformation properties of the molecular integrals under infinitesimal rotations. The paper has been recently published in: J. Chem. Phys. 75, 3962 (1981). A preprint of this paper is found in the Appendix to this interim report. While the study in this paper finds additional simplifying relationships among the derivatives of the integrals, analogous to the ones arising from translational invariance as discussed by Komornicki et al⁽²⁾ and Dupuis et al⁽³⁾, the numerical advantages that can be derived in practice by use of the additional relationships have not yet been explored.

While the Kahn SPDF ECP integral program was the first program with the capability to allow up to f-projection operators in the ECP and up to f-type GTO's, it was written with reliability and accuracy in mind more than efficiency. A recent independent version of the ECP integral

program, written by McMurchie and Davidson, is reported to be slower by a factor of 2. Thus, the Kahn SPDF ECP program remains the most efficient one of its kind despite the absence of the deliberate pursuit of efficiency in its design. The major source of inefficiency arises from the neglect of the use of the shell structure of the GTO's. This causes the computation of ECP integrals sometimes to be of comparable length to that of the two-electron integrals (evaluated over shells). This, however, has been of no consequence in past applications of the ECP method because the basis sets in use with the ECP method were so reduced over standard basis sets that the overall computation times had become trivial to begin with. Nonetheless, as the size of the molecular problems studied with the ECP method becomes larger, as in the study of metal atom clusters here considered, the basis sets again become large. The need to improve the efficiency of the SPDF ECP integral program for these applications by reorganizing the calculations around the shell approach is therefore increasingly imperative.

The organization of the SPDF ECP integral calculation around the shell approach is found not to be straightforward. The general ECP integral formulae have been shown by Kahn et al⁽¹⁾ to be as follows:

$$\begin{aligned}
 \langle n_c | U_L(\lambda_A) | n'_0 \rangle = & 4\pi \exp\left(-\frac{\zeta_c \zeta_0}{\zeta_c + \zeta_0} \bar{C} \bar{D}^2\right) \exp\left(-(\zeta_c + \zeta_0) \bar{D} \bar{A}^2\right) \sum_{\lambda=0}^{n_1 n'_1} \sum_{\mu=\lambda}^{-\lambda} \sum_{k_x=0}^{n_x} \sum_{k_y=0}^{n_y} \sum_{k_z=0}^{n_z} \sum_{k'_x=0}^{n'_x} \sum_{k'_y=0}^{n'_y} \sum_{k'_z=0}^{n'_z} \\
 & \cdot Z_{\lambda \mu}(\bar{D} \bar{A}) A_{k_x}^{n_x - k_x} A_{k_y}^{n_y - k_y} A_{k_z}^{n_z - k_z} A_{k'_x}^{n'_x - k'_x} A_{k'_y}^{n'_y - k'_y} A_{k'_z}^{n'_z - k'_z} \\
 & \cdot \begin{pmatrix} n_x \\ k_x \end{pmatrix} \begin{pmatrix} n_y \\ k_y \end{pmatrix} \begin{pmatrix} n_z \\ k_z \end{pmatrix} \begin{pmatrix} n'_x \\ k'_x \end{pmatrix} \begin{pmatrix} n'_y \\ k'_y \end{pmatrix} \begin{pmatrix} n'_z \\ k'_z \end{pmatrix} \int_{\Omega} Z_{\lambda \mu}(\Omega) \hat{x}^{k_x + k'_x} \hat{y}^{k_y + k'_y} \hat{z}^{k_z + k'_z} d\Omega \\
 & \cdot \int_0^{\infty} e^{-(\zeta_c + \zeta_0) \lambda^2} M_{\lambda}(2(\zeta_c + \zeta_0) \bar{D} \bar{A} \lambda) U_L^{(CORR)}(\lambda) \lambda^{k_x + k_y + k_z + k'_x + k'_y + k'_z + 2} d\lambda \quad (1)
 \end{aligned}$$

and

$$\langle n_c | \sum_{l=0}^{L-1} \sum_{m=l}^{L-l} |lm, A\rangle [U_y(\lambda_A) - U_L(\lambda_A)] \langle lm, A | | n'_0 \rangle = 16\pi^2 \exp(-\zeta_c \bar{C} \bar{A}^2 - \zeta_0 \bar{D} \bar{A}^2) \sum_{l=0}^{L-1} \sum_{m=l}^{L-l}$$

$$\begin{aligned}
& \sum_{\lambda=0}^{\ell+n} \sum_{\mu=\lambda}^{\lambda} \sum_{k_x=0}^{n_x} \sum_{k_y=0}^{n_y} \sum_{k_z=0}^{n_z} Z_{\lambda\mu}(\hat{CA}) A_{k_x}^{n_x-k_x} A_{k_y}^{n_y-k_y} A_{k_z}^{n_z-k_z} \left| \begin{matrix} n_x \\ k_x \end{matrix} \right| \left| \begin{matrix} n_y \\ k_y \end{matrix} \right| \left| \begin{matrix} n_z \\ k_z \end{matrix} \right| \int_{\Omega} Z_{\lambda\mu}(\Omega) x^{k_x} y^{k_y} z^{k_z} Z_{\lambda\mu}(\Omega) d\Omega \\
& \cdot \sum_{\lambda'=0}^{\ell+n'} \sum_{\mu'=\lambda'}^{\lambda'} \sum_{k'_x=0}^{n'_x} \sum_{k'_y=0}^{n'_y} \sum_{k'_z=0}^{n'_z} Z_{\lambda'\mu'}(\hat{BA}) A_{k'_x}^{n'_x-k'_x} A_{k'_y}^{n'_y-k'_y} A_{k'_z}^{n'_z-k'_z} \left| \begin{matrix} n'_x \\ k'_x \end{matrix} \right| \left| \begin{matrix} n'_y \\ k'_y \end{matrix} \right| \left| \begin{matrix} n'_z \\ k'_z \end{matrix} \right| \int_{\Omega} Z_{\lambda'\mu'}(\Omega) x^{k'_x} y^{k'_y} z^{k'_z} Z_{\lambda\mu}(\Omega) d\Omega \\
& \cdot \int_0^\infty e^{-(\xi_x+\xi_y)\lambda^2} M_\lambda(2\xi_x \bar{CA}\lambda) M_\lambda(2\xi_y \bar{BA}\lambda) [U_\ell^{\cos}(\lambda) - U_\ell^{\cos}(\lambda)] r^{k_x+k_y+k_z+k'_x+k'_y+k'_z+2} d\lambda. \quad (2)
\end{aligned}$$

The obvious problem is that these formulae do not exhibit the needed distinction of terms as being common to the components of a shell from those that change from component to component.

The first step taken to reexpress the integral formulae in a more shell-oriented structure was to find an alternative indexing system for the basic Gaussian-type orbitals (GTO's). Conventionally, each GTO is indexed by the set of "quantum numbers" (n_x, n_y, n_z) that determine the angular dependence of the GTO as in

$$|n_x, n_y, n_z, \xi\rangle = N x^{n_x} y^{n_y} z^{n_z} e^{-\xi r^2}. \quad (3)$$

An alternative indexing system is needed that is more explicit about the shell characteristics. It is found in the new set of "quantum numbers" (n, λ, μ) ; these are simply related to the old (n_x, n_y, n_z) "quantum numbers" by

$$n = n_x + n_y + n_z \quad (4a)$$

$$\lambda = n_x + n_y \quad (4b)$$

$$\mu = n_x - n_y \quad (4c)$$

The first index, n , is but the shell angular-momentum quantum number, and it remains the same for all components of a shell. One can range over all the "quantum numbers" (n_x, n_y, n_z) of a given shell just by changing the λ and μ "quantum numbers" as follows

$$(n, \lambda, \mu) \quad , \quad \lambda = 0, 1, 2, \dots, n \quad ; \quad \mu = -\lambda, \lambda, 2 \quad . \quad (5)$$

In turn, the (n_x, n_y, n_z) "quantum numbers" are obtained from (n, λ, μ) "quantum numbers" by

$$n_x = \frac{1}{2}(\lambda + \mu) \quad (6a)$$

$$n_y = \frac{1}{2}(\lambda - \mu) \quad (6b)$$

$$n_z = n - \lambda \quad . \quad (6c)$$

As an example, we give the indexes for the components of the f-shell below:

n	λ	μ	n_x	n_y	n_z
3	0	0	0	0	3
3	1	-1	0	1	2
3	1	1	1	0	2
3	2	-2	0	2	1
3	2	0	1	1	1
3	2	2	2	0	1
3	3	-3	0	3	0
3	3	-1	1	2	0
3	3	1	2	1	0
3	3	3	3	0	0

The simplicity and order in the (n, λ, μ) indexing system over that of the (n_x, n_y, n_z) indexing system becomes apparent upon even a casual inspection of this f-shell case. The simplicity of the new indexing system is demonstrated, for example, in the ease with which the number of components of a shell can be calculated, i.e.

$$\sum_{\lambda=0}^n \sum_{\mu=-\lambda}^{\lambda} = \frac{1}{2} (n+1)(n+2) \quad (7)$$

The properties of the GTO's relevant to the ECP integrals must now be found in terms of the (n, λ, μ) index system to enable the reformulation of the integral formulae. Consider in particular the angular dependence factor

$$X_{n,\lambda,\mu} = x^{n_x} y^{n_y} z^{n_z} . \quad (8)$$

The translation of x, y , or z from center C onto center A is

$$x_c = x_A + AC_x \quad (9a)$$

$$y_c = y_A + AC_y \quad (9b)$$

$$z_c = z_A + AC_z . \quad (9c)$$

The expansion of the angular dependence factor $X_{n,\lambda,\mu}$ from center C onto center A induced by this translation can be worked out straightforwardly for any particular case given (n, λ, μ) . For example, for $(2, 2, 0)$ one finds

$$x_c y_c = x_A y_A + AC_x y_A + AC_y x_A + AC_x AC_y . \quad (10)$$

The general expression, however, is considerably more difficult to find. We have found a general expression that shows the expansion terms in the new (n, λ, μ) "quantum number" system, as follows

$$X_{n,\lambda,\mu}(x_c) = \sum_{\bar{n}=0}^n \sum_{\bar{\lambda}=\bar{\lambda}_0}^{\bar{\lambda}_1} \sum_{\bar{\mu}=\bar{\mu}_0}^{\bar{\mu}_1} B_{\bar{n},\bar{\lambda},\bar{\mu}}^{n,\lambda,\mu} X_{n-\bar{n},\lambda-\bar{\lambda},\mu-\bar{\mu}}^{(AC)} X_{\bar{n},\bar{\lambda},\bar{\mu}}(x_A) \quad (11)$$

where

$$\bar{\lambda}_0 = \max(0, \bar{n} + \lambda + n) , \quad (12a)$$

$$\bar{\lambda}_1 = \min(\lambda, \bar{n}) . \quad (12b)$$

$$\bar{\mu}_0 = \max(-\bar{\lambda}, \bar{\lambda} + \mu - \lambda). \quad (13a)$$

and

$$\bar{\mu}_1 = \min(\bar{\lambda}, -\bar{\lambda} + \mu + \lambda). \quad (13b)$$

In this formula, the coefficient of the expansion is just a product of binomial coefficients,

$$B_{\bar{n}, \bar{\lambda}, \bar{\mu}}^{n, \lambda, \mu} = \begin{pmatrix} n_x \\ \bar{n}_x \end{pmatrix} \begin{pmatrix} n_y \\ \bar{n}_y \end{pmatrix} \begin{pmatrix} n_z \\ \bar{n}_z \end{pmatrix}. \quad (14)$$

The integral formulae may now be reexpressed in terms of the new GTO (n, λ, μ) indexing system. Let us first define the basic radial integrals

$$I_{n; \ell} = \exp(-(\zeta_c + \zeta_b) \bar{\Delta} \lambda^2) \int_0^\infty e^{-(\zeta_c + \zeta_b) \lambda^2} M_\ell(2(\zeta_c + \zeta_b) \bar{\Delta} \lambda) U_\ell(\lambda) \lambda^{n+2} d\lambda \quad (15)$$

and

$$J_{n; \ell', \ell}^{(\ell)} = \exp(-\zeta_c \bar{\Delta} \lambda^2 - \zeta_b \bar{\Delta} \lambda^2) \int_0^\infty e^{-(\zeta_c + \zeta_b) \lambda^2} M_{\ell'}(2\zeta_c \bar{\Delta} \lambda) M_\ell(2\zeta_b \bar{\Delta} \lambda) [U_{\ell'} - U_\ell] \lambda^{n+2} d\lambda. \quad (16)$$

The ECP matrix element of the first kind, apart from GTO normalization factors, is

$$\langle n_0 | U_\ell(\lambda_n) | n'_0 \rangle = 4\pi \exp\left(-\frac{\zeta_c \zeta_b}{\zeta_c + \zeta_b} \bar{\Delta} \lambda^2\right) \sum_{\ell=0}^{n, n'} \sum_{\ell'=0}^{2n} I_{\ell; \ell} C_{\ell; \ell} \quad n \geq n' \quad (17)$$

where the coefficient of the I radial integral is

$$c_{p;l} = \sum_{q=0}^p \theta_{q,p-q;l} \quad 0 \leq p \leq n' \quad (18a)$$

$$= (1 - \delta_{n,n'}) \sum_{q=p-n'}^p \theta_{q,p-q;l} \quad n'+1 \leq p \leq n \quad (18b)$$

$$= \sum_{q=n-n'}^{2n-p} \theta_{p+q-n,n-q;l} \quad n+1 \leq p \leq 2n \quad (18c)$$

and the basic $\theta_{\kappa,\kappa';l}$ elements are defined as

$$\begin{aligned} \theta_{\bar{n},\bar{n}';l} &= \sum_{\bar{\lambda}=\bar{\lambda}_0}^{\bar{\lambda}_1} \sum_{\bar{\mu}=\bar{\mu}_0}^{\bar{\mu}_1} \theta_{\bar{n},\bar{\lambda},\bar{\mu}}^{n,\lambda,\mu} \chi_{n-\bar{n},\lambda-\bar{\lambda},\mu-\bar{\mu}}^{(AC)} \sum_{\bar{\lambda}'=\bar{\lambda}'_0}^{\bar{\lambda}'_1} \sum_{\bar{\mu}'=\bar{\mu}'_0}^{\bar{\mu}'_1} \theta_{\bar{n}',\bar{\lambda}',\bar{\mu}'}^{n',\lambda',\mu'} \chi_{n'-\bar{n}',\lambda'-\bar{\lambda}',\mu'-\bar{\mu}'}^{(AB)} \\ &\cdot \sum_{m=0}^l \bar{Z}_{l,m}(\hat{\alpha}) \int_{\Omega} \chi_{\bar{n},\bar{\lambda},\bar{\mu}}(\hat{x}) \bar{Z}_{l,m}(\hat{x}) \chi_{\bar{n}',\bar{\lambda}',\bar{\mu}'}(\hat{x}) d\Omega \end{aligned} \quad (19)$$

The ECP matrix element of the second kind, apart from GTO normalization factors, is

$$\langle n_c | \sum_{l=0}^L \sum_{m=0}^l |lm,A\rangle [U_2(\lambda_A) - U_1(\lambda_A)] \langle lm,A || n'_c \rangle = 16\pi^2 \sum_{l=0}^{L-1} \sum_{l'=0}^{l+n} \sum_{l''=0}^{l+n'} \sum_{p=0}^{2n} J_{p;l,l',l''}^{(l)} c_{p;l',l''}^{(l)} \quad (20)$$

where the coefficient of the J radial integral is

$$c_{p;l',l''}^{(l)} = \sum_{q=0}^p \xi_{q,p-q;l',l''}^{(l)} \quad 0 \leq p \leq n' \quad (21a)$$

$$= (1 - \delta_{n,n'}) \sum_{q=p-n'}^p \xi_{q,p-q;l',l''}^{(l)} \quad n'+1 \leq p \leq n \quad (21b)$$

$$= \sum_{q=n-n'}^{2n-p} \xi^{(l)}_{p+q-n, n-q; l', l''} \quad n+1 \leq p \leq 2n \quad (21c)$$

and the basic $\xi^{(l)}_{\bar{n}, \bar{n}'; l', l''}$ elements are defined as

$$\begin{aligned} \xi^{(l)}_{\bar{n}, \bar{n}'; l', l''} &= \sum_{\bar{\lambda}=\bar{\lambda}_0}^{\bar{\lambda}_1} \sum_{\bar{\mu}=\bar{\mu}_0}^{\bar{\mu}_1} B_{\bar{n}, \bar{\lambda}, \bar{\mu}}^{n, \lambda, \mu} X_{n-\bar{n}, \lambda-\bar{\lambda}, \mu-\bar{\mu}}^{(AC)} \\ &\quad \sum_{\bar{\lambda}'=\bar{\lambda}'_0}^{\bar{\lambda}'_1} \sum_{\bar{\mu}'=\bar{\mu}'_0}^{\bar{\mu}'_1} B_{\bar{n}', \bar{\lambda}', \bar{\mu}'}^{n', \lambda', \mu'} X_{n'-\bar{n}', \lambda'-\bar{\lambda}', \mu'-\bar{\mu}'}^{(AB)} \\ &\quad \sum_{m'=l'}^{l'} Z_{l', m'}^{(\hat{C}A)} \sum_{m''=l''}^{l''} Z_{l'', m''}^{(\hat{B}A)} \sum_{m=l}^{l'} \int_{\Omega} Z_{l', m'} X_{\bar{n}, \bar{\lambda}, \bar{\mu}}^{l, m} Z_{l'', m''} X_{\bar{n}', \bar{\lambda}', \bar{\mu}'}^{l', m'} Z_{l, m} d\Omega \quad (22) \end{aligned}$$

The Z_{lm} are the real spherical harmonics.

The new ECP integral formulae, Equations (17) and (20), replace the old formulae given by Equations (1) and (2). The principal result in Equations (17) and (20) is that the I and J radial integrals are shown to be common to all the components of a shell. Because radial integrals are often quite time consuming to calculate, this result alone shows these new formulae to yield the desired simplification that is the promise of the shell approach. All the terms that depend on the detailed geometry are collected in the C coefficients; these coefficients appear to be fully dependent on the properties of the individual components, although we have not yet concluded the analysis.

One very important simplification has come to light upon extensively exercising a computer-driven loop through the various angular integrals appearing in both the E and E elements, Equations (19) and (22): the majority of these angular integrals are zero! The remaining task is to identify precisely all the selection rules for these angular integrals so that only the non-vanishing terms in the D and E elements are ultimately evaluated. After the analysis is complete, it is planned to implement these new formulae. This

will require the complete revision of many of the routines in the current SPDF ECP integral program since the structure of the formulae is completely different from the previous formulation. The basic interface with Komornicki's program, however, is expected to remain essentially unaltered, thereby making this upgrade compatible with the work already done.

Improvements in the ECP's

A new unified approach to the calculation of the "shape-and-Hamiltonian-consistent" ECP's has been derived; it contains the "shape-consistent" approach of Christiansen et al.⁽⁴⁾ as a special case, and it deals directly with the essential orbital properties that in turn ensure the matching of the valence-valence interactions in the approach of Rappé et al.⁽⁵⁾. The foundation of this unified approach lies in the formulation of the atomic energy in terms of moment-accumulation functions as presented by Kahn⁽⁶⁾ at the recent NRCC-sponsored workshop on Effective Potential Methods. More details will be presented in the final report on this project.

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APPENDIX A

"RELATIONSHIPS AMONG DERIVATIVES OF THE INTEGRALS IN THE
CALCULATION OF THE GRADIENT OF THE ELECTRONIC ENERGY
WITH RESPECT TO THE NUCLEAR COORDINATES"

Relationships among derivatives of the integrals in the calculation
of the gradient of the electronic energy with respect
to the nuclear coordinates

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ABSTRACT

The use of the translational invariance property of molecular integrals is extended by its combination with the closely related transformation properties under infinitesimal rotations. This further reduces the number of truly linearly independent derivatives of the molecular integrals that require explicit calculation in obtaining the gradient of the electronic energy. The detailed linear equations that yield the linearly dependent derivatives in terms of the "independent" derivatives are presented.

I. INTRODUCTION

The usefulness of the gradient of the molecular electronic energy with respect to the nuclear coordinates ranks close in importance to that of the electronic energy itself. The gradient yields an immediate sense of the local topography about any point on the potential energy surface for a chemical reaction. It enables, moreover, the efficient and systematic convergence to the points at which the energy surface is stationary with respect to variation of the nuclear coordinates.⁽¹⁻⁶⁾ This is especially useful in multidimensional cases in which physical intuition may be of limited value in helping to locate these critical points.

The techniques for the accurate calculation of the gradient of the molecular electronic energy have been actively developed and refined in recent years.⁽⁷⁻¹⁹⁾ The computational effort required to calculate the gradient, notwithstanding these recent important advances, is not a minor one. Both Komornicki et al⁽¹¹⁾ and Dupuis et al⁽¹⁵⁾, for example, find that, on the average, the calculation of the gradient requires about 2-1/2 times the computational effort of the calculation of the energy itself.

Apart from simple overlap integrals, the expression for the gradient of the electronic energy differs from that for the energy by the replacement of the integrals over atomic basis functions by the derivatives of these integrals with respect to the nuclear coordinates. Consider, for illustrative purposes, the case of a closed-shell system in the single determinant approximation. The electronic energy is⁽²⁰⁾

$$E = \sum_i c_i^\dagger \left(2H^{(0)} + G^{(0)} \right) c_i \quad (1)$$

The ξ_i vector contains the expansion coefficients of the i 'th molecular orbital (MO) in the atomic basis functions. The summation in Eq. (1) ranges over all occupied MO's. The elements of the $H_{\sim}^{(0)}$ matrix are the one-electron integrals, and $G_{\sim}^{(0)}$ is the matrix of Coulomb and exchange two-electron integrals in the well-known form

$$G_{\sim}^{(0)} = 2 \sum_j \xi_j^\dagger B \xi_j \quad (2)$$

where the elements of the supermatrix B are

$$B_{\mu, \nu; \kappa, \lambda} = [\mu\nu|\kappa\lambda] - \frac{1}{4} [\mu\kappa|\nu\lambda] - \frac{1}{4} [\mu\lambda|\nu\kappa] \quad (3)$$

The $[\mu\nu|\kappa\lambda]$ term, for example, is a basic two-electron integral over atomic basis functions.⁽²¹⁾ Let the α 'th component ($\alpha = x, y, z$) of the coordinates of the k 'th atom be denoted as $P_{k, \alpha}$. The partial derivative of the electronic energy with respect to $P_{k, \alpha}$ has been shown by Moccia⁽⁷⁾ and Fletcher⁽⁸⁾ to be given by

$$\frac{\partial E}{\partial P_{k, \alpha}} = \sum_i \xi_i^\dagger (2 H_{\sim}^{(1)} + G_{\sim}^{(1)} - \epsilon_i S_{\sim}^{(1)}) \xi_i \quad (4)$$

where

$$H_{\sim}^{(1)} = \frac{\partial H_{\sim}^{(0)}}{\partial P_{k, \alpha}} \quad (5)$$

and

$$G_{\sim}^{(1)} = 2 \sum_j \xi_j^\dagger \frac{\partial B}{\partial P_{k, \alpha}} \xi_j \quad (6)$$

and

$$S_{\sim}^{(1)} = \frac{\partial S_{\sim}}{\partial P_{k, \alpha}} \quad (7)$$

The elements of the S_{\sim} matrix are just the overlap integrals. Thus, the calculation of the gradient of the electronic energy is seen from

this example, to revolve about the calculation and assembly of the derivatives of the one-electron integrals, the derivatives of the two-electron integrals, and the derivatives of the overlap integrals, Eqs. (5), (6) and (7) respectively.

In this paper we discuss relationships that exist among the various derivatives of each integral required in the calculation of the gradient of the electronic energy. These relationships derive from the spatial-transformation properties of the integrals independently of the existence of spatial symmetry in the molecular system as a whole. The specific spatial-transformation properties of interest here derive from the molecular integrals under infinitesimal translations⁽²²⁾ and rotations.⁽²³⁾ The use of the property of translational invariance alone was first proposed by Komornicki et al.⁽¹⁾ and later extended by Dupuis et al.⁽¹⁵⁾ Whereas the translational invariance property has been used to obtain significant simplifications in the calculation of the gradient of the electronic energy, no use has been made of the closely related transformation properties under infinitesimal rotations. Dupuis et al have, in passing, commented on the special condition of rotational invariance when only s-type basis functions appear in the integrals but made no use of it.⁽¹⁵⁾ We show in this work the additional relationships among the derivatives of the integrals that can be derived from the combined use of the properties of the integrals under infinitesimal translational and rotational transformations. We find that the six conditions that result from the transformation properties taken together reduce the number of linearly independent derivatives from 12 to 6 in the case of a four-center integral, and from 9 to 3 in the case of a three-center integral. In a two-center case, the number of linearly independent derivatives is reduced from 6 to 1. The number of derivative integrals that require explicit calculation in the evaluation of the gradient of the

electronic energy are found to be considerably reduced, in principle, by the linear relationships among them. These linear relationships are found from the transformation properties of molecular integrals under infinitesimal translations and rotations.

II. RELATIONSHIPS AMONG THE DERIVATIVES OF A MOLECULAR INTEGRAL WITH RESPECT TO THE NUCLEAR COORDINATES

Let us denote an integral by the symbol I and, although we are concerned at most with a four-center case, let us assume, for the sake of generality, that the integral is an N -center case. We indicate this by writing $I(p_1, p_2, \dots, p_N)$. The integral must be translationally invariant.⁽²²⁾ Therefore, we may write

$$I(p_1, p_2, \dots, p_N) = I(p_1 - \vec{T}, p_2 - \vec{T}, \dots, p_N - \vec{T}) \quad (8)$$

where \vec{T} is an arbitrary three dimensional vector. Let \vec{T} be an infinitesimal translation vector, and expand the right side of Eq. (8) in a Taylor series to obtain

$$I(p_1, p_2, \dots, p_N) = I(p_1, p_2, \dots, p_N) - \sum_{\alpha=x,y,z} T_\alpha \sum_{k=1}^N \frac{\partial I}{\partial p_{k,\alpha}} + \dots \quad (9)$$

Equating linearly independent terms results in conditions on the partial derivatives of I to all orders. The condition on the first-order partial derivatives of I , the same as previously discussed by Komornicki et al is found to be

$$\sum_{k=1}^N \frac{\partial I}{\partial p_{k,\alpha}} = 0 \quad \alpha = x, y, z \quad (10)$$

We consider next the additional conditions on the first-order partial derivatives of I resulting from the transformation properties of I under infinitesimal rotations. We define the infinitesimal rotation, \hat{R} , by

$$\hat{R}P_{k,\alpha} = \sum_{\beta=x,y,z} (\delta_{\alpha,\beta} + \epsilon_{\alpha,\beta}) P_{k,\beta} \quad \alpha = x,y,z \quad (11)$$

where $\epsilon_{\alpha,\beta}$ are the infinitesimal matrix elements of an antisymmetric matrix⁽²⁴⁾,

$$\epsilon_{\alpha,\beta} = -\epsilon_{\beta,\alpha} \quad (12)$$

The integrand of the I integrals depends on the nuclear coordinates $\{P_k\}$ through both operators and basis functions, each centered on one of these nuclear coordinates. The nuclear attraction operators are the only operators explicitly dependent on the nuclear coordinates in the integrals appearing in the calculation of the electronic energy. Since these operators are spherically symmetric about their respective nuclei, the transformation properties of the I integrals upon an infinitesimal rotation are solely determined by the transformation properties of the basis functions.

We take the basis functions to be Cartesian Gaussian basis functions⁽²⁵⁾

$$G_{n_x, n_y, n_z}(r) = N(\zeta, n_x, n_y, n_z) x^{n_x} y^{n_y} z^{n_z} e^{-\zeta r^2} \quad (13)$$

where $N(\zeta, n_x, n_y, n_z)$ is the normalization constant. These functions are usefully grouped by shells. The functions in the same shell have the property that, in addition to the exponential parameter ζ , the sum $n = n_x + n_y + n_z$ is the same. The transformation properties of these basis functions upon an infinitesimal rotation, Eq. (11), are

$$G_{n_x, n_y, n_z}(\hat{R}r) = G_{n_x, n_y, n_z}(r) + \sum_{\alpha > \beta} \epsilon_{\alpha,\beta} \delta G_{\alpha,\beta}(r) + \dots \quad (14)$$

where

$$\delta G_{y,x} = A_{y,x} G_{n_x+1, n_y-1, n_z} - A_{x,y} G_{n_x-1, n_y+1, n_z} \quad (15a)$$

$$\delta G_{z,x} = A_{z,x} G_{n_x+1, n_y, n_z-1} - A_{x,z} G_{n_x-1, n_y, n_z+1} \quad (15b)$$

$$\delta G_{z,y} = A_{z,y} G_{n_x, n_y+1, n_z-1} - A_{y,z} G_{n_x, n_y-1, n_z+1} \quad (15c)$$

and

$$A_{\alpha, \beta} = n_{\alpha} \left(\frac{2n_{\beta} + 1}{2n_{\alpha} - 1} \right)^{1/2} \quad \alpha, \beta = x, y, z \quad (15d)$$

Equations (14) and (15) show that, upon an infinitesimal rotation, a basis function transforms into other functions of the same shell. The integrand of I consists, apart from the usual operators, of a product of these basis functions. The transformation properties of the integral I under an infinitesimal rotation are, consequently, found to be

$$\begin{aligned} I(\hat{R}P_1, \hat{R}P_2, \dots, \hat{R}P_N) &= I(P_1, P_2, \dots, P_N) \\ &+ \sum_{\alpha > \beta} \sum \epsilon_{\alpha, \beta} \delta I_{\alpha, \beta}(P_1, P_2, \dots, P_N) + \dots \end{aligned} \quad (16)$$

where

$$\delta I_{\alpha, \beta} = \sum_{\ell} \delta I_{\alpha, \beta}^{(\ell)} \quad (17)$$

The summation in Eq. (17) ranges over all basis functions appearing in the integrand of I. The term $\delta I^{(\ell)}$ is defined as an I integral in which the ℓ 'th basis function, G_{n_x, n_y, n_z} , has been replaced by a function $\delta G_{\alpha, \beta}$ defined by Eqs. (15a) - (15c). Consequently, each integral $\delta I_{\alpha, \beta}^{(\ell)}$ is just a simple linear combination of two I-type of integrals, as follows

$$\delta I_{y,x}^{(\ell)} = A_{y,x} I_{n_x+1, n_y-1, n_z}^{(\ell)} - A_{x,y} I_{n_x-1, n_y+1, n_z}^{(\ell)} \quad (18a)$$

$$\delta I_{z,x}^{(\ell)} = A_{z,x} I_{n_x+1, n_y, n_z-1}^{(\ell)} - A_{x,z} I_{n_x-1, n_y, n_z+1}^{(\ell)} \quad (18b)$$

$$\delta I_{z,y}^{(l)} = A_{z,y} I_{n_x, n_y+1, n_z-1}^{(l)} - A_{y,z} I_{n_x, n_y-1, n_z+1}^{(l)} \quad (18c)$$

The notation $I_{n'_x, n'_y, n'_z}^{(l)}$, analogously to its use in $\delta I_{\alpha, \beta}^{(l)}$, denotes an I integral in which the l 'th basis function, G_{n_x, n_y, n_z} , has been replaced by another basis function, $G_{n'_x, n'_y, n'_z}$. Note that the replacement functions belong to the same shell as the original function.

The effect of an infinitesimal rotation can also be expressed as

$$I(\hat{R}_{\hat{n}_1}^P, \hat{R}_{\hat{n}_2}^P, \dots, \hat{R}_{\hat{n}_N}^P) = I(P_{\hat{n}_1} + \epsilon_{\hat{n}_1}^P, P_{\hat{n}_2} + \epsilon_{\hat{n}_2}^P, \dots, P_{\hat{n}_N} + \epsilon_{\hat{n}_N}^P) \quad (19)$$

Expanding the right side of Eq. (20) in a Taylor series, and using the antisymmetry property of the ϵ matrix, one obtains

$$I(\hat{R}_{\hat{n}_1}^P, \hat{R}_{\hat{n}_2}^P, \dots, \hat{R}_{\hat{n}_N}^P) = I(P_1, P_2, \dots, P_N) + \sum_{\alpha > \beta} \sum \epsilon_{\alpha, \beta} \left[\sum_{k=1}^N \left(P_{k, \beta} \frac{\partial I}{\partial P_{k, \alpha}} - P_{k, \alpha} \frac{\partial I}{\partial P_{k, \beta}} \right) \right] + \dots \quad (20)$$

We equate each linearly independent set of terms in this result with those obtained in Eq. (16). This yields the conditions on the first-order partial derivatives of I that derive from the transformation properties under infinitesimal rotations. One obtains

$$\sum_{k=1}^N \left(P_{k, \beta} \frac{\partial I}{\partial P_{k, \alpha}} - P_{k, \alpha} \frac{\partial I}{\partial P_{k, \beta}} \right) = \delta I_{\alpha, \beta} \quad \alpha, \beta = y, x; z, x; z, y \quad (21)$$

It follows from Eqs. (18a) - (18c) that the right side of Eq. (21) is zero in the special case when all the basis functions appearing in I are s-type functions, $n_x = n_y = n_z = 0$. Equation (21) reduces in that special case to a condition of rotational invariance⁽¹⁵⁾.

Taken together, Eqs. (10) and (21) constitute the six conditions relating, in general, the first-order partial derivatives of an arbitrary molecular integral I to each other. There are many possible ways to combine Eqs. (10) and (21). One particular combination to be used later is

$$\sum_{k=1}^{N-1} \left[(P_{k,B} - P_{N,B}) \frac{\partial I}{\partial P_{k,\alpha}} - (P_{k,\alpha} - P_{N,\alpha}) \frac{\partial I}{\partial P_{k,B}} \right] = \delta I_{\alpha,B}$$

$$\alpha, B = y, x; z, x; z, y \quad (22)$$

The gradient of I has $3N$ components. One can always obtain $(3N-6)$ of these by independent explicit calculation and then, it would seem at first, that one could obtain the remaining six components by straightforwardly solving the system of linear equations. A closer inspection reveals, however, that the rank of the coefficient matrix of the reduced system of linear equations depends on the choice of the $(3N-6)$ "independent" components. We therefore discuss three important applications of Eqs. (10) and (21) separately.

A. Gradients of Two-Center Integrals

The gradient of the two-center integral has six components. Since there are also 6 conditions, Eqs. (10) and (21), relating the six components to each other, one would at first conclude that these equations alone fully define all the components of the gradient. A reduction of the coefficient matrix of the system of linear equations to canonical form, however, shows that the rank of this matrix⁽²⁴⁾ is actually only 5. Thus, one of the six components of the gradient may be considered truly independent. We choose this one to be $\partial I / \partial P_{1,x}$, for example, since the choice

is immaterial in this case. Assuming that $P_{1,x} \neq P_{2,x}$, the remaining 5 components of the gradient are obtained as

$$\frac{\partial I}{\partial P_{1,\alpha}} = \frac{1}{(P_{1,x} - P_{2,x})} \left[(P_{1,\alpha} - P_{2,\alpha}) \frac{\partial I}{\partial P_{1,x}} + \delta I_{\alpha,x} \right] \quad \alpha = y, z \quad (23)$$

$$\frac{\partial I}{\partial P_{2,\alpha}} = - \frac{\partial I}{\partial P_{1,\alpha}} \quad \alpha = x, y, z \quad (24)$$

B. Gradients of Three-Center Integrals

The gradient of the three-center integral has nine components. The rank of the coefficient matrix of the linear equations relating these nine components can be shown to be 6. We exclude for the purpose of this discussion the special case of collinear geometries. In this special case the rank of the coefficient matrix is 5. Moreover, because of the special geometry, the number of implicit independent variables is reduced as well. Excluding the collinear case, three of the nine components of the gradient may hence be taken as "independent" components. Not every choice of these three components, however, yields a system of linear equations of rank 6. Examples of choices of the three components that lead to a rank lower than 6 are

$$\left(\frac{\partial I}{\partial P_{k,x}}, \frac{\partial I}{\partial P_{k,y}}, \frac{\partial I}{\partial P_{k,z}} \right) \quad k = 1, 2, 3 \quad (25)$$

and

$$\left(\frac{\partial I}{\partial P_{1,\alpha}}, \frac{\partial I}{\partial P_{2,\alpha}}, \frac{\partial I}{\partial P_{3,\alpha}} \right) \quad \alpha = x, y, z \quad (26)$$

A choice of three independent components that preserves the rank of 6 should include at least two different centers, and, if three different centers are present, at least two different types of cartesian

components. Of the many possible choices that satisfy these requirements, we shall use the following

$$\left(\frac{\partial I}{\partial P_{1,x}}, \frac{\partial I}{\partial P_{1,y}}, \frac{\partial I}{\partial P_{2,z}} \right) \quad (27)$$

The equations that follow are therefore only representative of the linear equations determining a set of "dependent" gradient components in terms of a counterpart choice of "independent" components.

It is convenient at this point to define a notation that will allow us to express in compact form the remaining equations. First we define the elements of a 3×3 matrix $\Delta_{k,l}$ as

$$\begin{pmatrix} 0 & -(P_{k,z} - P_{N,z}) & (P_{l,y} - P_{N,y}) \\ -(P_{k,z} - P_{N,z}) & 0 & (P_{l,x} - P_{N,x}) \\ -(P_{k,y} - P_{N,y}) & (P_{k,x} - P_{N,x}) & 0 \end{pmatrix} \quad (28)$$

where N is equal to 3 in the three-center integral case. Second, we define the components of a three dimensional vector $g_{k,l}$ as

$$\left(\frac{\partial I}{\partial P_{k,x}}, \frac{\partial I}{\partial P_{k,y}}, \frac{\partial I}{\partial P_{l,z}} \right) \quad (29)$$

Note, for example, that Expression (27) gives the components of a $g_{1,2}$ vector, and that $g_{1,2} + g_{2,1} = g_{1,1} + g_{2,2}$. Lastly, we define the components of another three dimensional vector δ as

$$\left(\delta I_{z,y}, \delta I_{z,x}, \delta I_{y,x} \right) \quad (30)$$

The elements of this vector have been in turn defined in Eqs. (17) and (18).

The "independent" components of the gradient have been chosen as the three elements of the $g_{1,2}$ vector, Expression (27). The remaining six components are contained in the vectors $g_{2,1}$ and $g_{3,3}$. These vectors are obtained in turn as the solutions to three simultaneous linear equations. Assuming $P_{2,z} \neq P_{3,z}$, these equations, in matrix notation, are

$$\hat{A}_{2,1} g_{2,1} = \hat{f} \quad (32)$$

$$g_{3,3} = -g_{1,2} - g_{2,1} \quad (33)$$

where the vector on the right side of Eq. (32), \hat{f} , is defined as

$$\hat{f} = \hat{A}_{1,2} g_{1,2} + \hat{g} \quad (34)$$

C. Gradients of Four-Center Integrals

The gradient of the four-center integral has 12 components. The rank of the coefficient matrix of the linear equations relating these 12 components can again be shown to be 6. Therefore, six out of the 12 components of the gradient may be taken as the "independent" components. A convenient (but not unique) choice of "independent" components that preserves the rank of 6 in the reduced linear equations are the elements of the two vectors $g_{1,1}$ and $g_{2,3}$. Assuming $P_{3,z} \neq P_{4,z}$ and excluding again the special case of collinear geometries, the equations giving the remaining components of the gradient are

$$\hat{A}_{3,2} g_{3,2} = \hat{f} \quad (35)$$

$$g_{4,4} = -g_{1,1} - g_{2,3} - g_{3,2} \quad (36)$$

The vector f on the right side of Eq. (35) is defined as

$$f = -A_{2,3}g_{2,3} - A_{1,1}g_{1,1} + \delta \quad (37)$$

The various $A_{k,l}$ matrices in this case contain N set equal to 4.

In the general case, the "independent" components may be taken as the vectors $g_{N-2,N-1}$ and $\{g_{k,k}, k = 1, N-3\}$. The remaining components of the gradient are contained in the vectors $g_{N-1,N-2}$ and $g_{N,N}$. Assuming $P_{N-1,z} \neq P_{N,z}$, these components are obtained from the equations

$$A_{N-1,N-2} g_{N-1,N-2} = f \quad (38)$$

$$g_{N,N} = - \sum_{k=1}^{N-3} A_{k,k} g_{k,k} - g_{N-2,N-1} - g_{N-1,N-2} \quad (39)$$

where the vector f on the right side of Eq. (38) is

$$f = -A_{N-2,N-1} g_{N-2,N-1} - \sum_{k=1}^{N-3} A_{k,k} g_{k,k} + \delta \quad (40)$$

III. CONCLUSION

The calculation of the gradient of the electronic energy requires the calculation of the derivatives with respect to the nuclear coordinates of the integrals over atomic basis functions. The number of these derivative integrals to be calculated is very large, particularly because of the two-electron type of integrals, of which there are more than $M^4/8$ in the case of M basis functions. We have shown that the condition of translational invariance of the integrals can be combined with the

conditions expressing the transformation properties of integrals under infinitesimal rotations to obtain equations that yield the "dependent" derivative integrals in terms of the "independent" ones. These equations are shown to be at most a set of three simultaneous linear equations. The existence of these interrelationships, in principle, reduce considerably the number of derivative integrals that require explicit calculation. The number of linearly independent derivatives is reduced from 12 to 6 for a four-center integral, from 9 to 3 for a three-center integral, and from 6 to 1 for a two-center integral independently of the existence of spatial symmetry in the molecular system as a whole.

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